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DMIC review OF RECENT DEVELOPMENTS

Corrosion and Compatibility

W. E. Berry December 17, 1969

ALUMINUM ALLOYS

Aqueous Corrosion

The corrosion behavior and response to cathodic protection of 19 aluminum alloys in seawater has been studied at the Naval Research Laboratory.(1) These alloys were exposed 368 days in quiescent seawater, and the mean electrode potential was determined over exposure periods ranging from 63 to 360 days. Alloys more positive than -0.89 V (versus Ag/AgCl electrode) exhibited severe corrosion and pitting. Alloys in this group included most (but not all) of the 2000 and 7000 series plus 1100-F, 3003-H14, and 6061-T6 alloys. Alloys whose mean electrode potentials were -0.92 to -1.24 V (Ag/AgCl) were resistant to both pitting and crevice corrosion. Included in this group were the 5000 series and X7005-T63, 7106-T63, 6061-T651, and 1100-H14 alloys. Cathodic protection was effective in reducing surface pitting and crevice corrosion to tolerable limits on all alloys except for edge cracking on the X7002-T6 and 7178-T6 alloys.

The effectiveness of coatings on aluminum alloys in preventing galvanic corrosion in couples with 347 CRES and Ti-6Al-4V has been reported by NASA.(2) Couples including sulfuric-acid- and chromic-acid-anodized and chromate-treated aluminum were exposed to salt spray. No galvanic corrosion occurred when the anodized coatings were not impaired, and hence, the thicker sulfuric acid coating was more resistant than the thinner chromic-acid-anodized film. The chromate conversion coating offered good protection to the environment, but being a good conductor, became part of a galvanic couple. The galvanic effects with Ti-6Al-4V alloy were much less than those with the 347 CRES because there is less electrochemical potential difference between titanium and aluminum than between 347 CRES and aluminum.

A review of the corrosion behavior of aluminum alloys in natural fresh and tap waters has been made by Reynolds Metals Company.(3) Included in the review are rankings according to the corrosivity towards 3003 alloy of municipal waters in major United States cities. Also included are some 135 references.

Stress-Corrosion Cracking

A program to develop an aluminum alloy with high strength, fracture toughness, and resistance to stress-corrosion cracking was completed by Alcoa.(4) Variations on the 7075 alloy composition were investigated. Preliminary results indicated that alloys containing either higher zinc or higher copper than normal in 7075 were more resistant to stress-corrosion cracking by 3 to 8 ksi than 7075 alloy. However, the strength obtainable in these alloys was affected by the rate of quench from solution-treating temperature. Substitution of manganese or zirconium for chromium in the alloy was recommended to overcome the quench sensitivity.

Fatigue-crack propagation of aluminum alloys in several environments was studied at Boeing.(5) Wedge-force and remote-loading techniques were employed in dry air (reference condition), humid air, distilled water, and 3.5 percent NaCl solution. Alloy 2024-T3 was relatively insensitive to the humid air and distilled water whereas 7075-T6 and 7178-T6 alloys showed a pronounced acceleration in fatigue-crack growth rate. All three alloys exhibited enhanced fatigue-crack growth rate in 3.5 percent NaCl solution. However, fatigue-crack growth of 7178-T6 was faster in distilled water than in 3.5 percent NaCl solution. This behavior was attributed to crack blunting due to the intergranular mode of fracture.

Rocketdyne has issued a final report on the effects of point defects on the stress-corrosion-cracking susceptibility of aluminum alloy 7075 in the -T6, -T73, and intermediate heat-treated conditions.(6) Point defects were introduced by irradiation to a fast neutron dosage of 0.8×10^{19} nvt. Tensile specimens stressed to 25, 50, and 75 percent of yield strength were subjected to alternate immersion in 3.5 percent NaCl solution. The irradiation caused a 50 percent reduction in the stress-corrosion-cracking failure time of 7075-T6, but appeared to have no effect on the other heat-treated conditions. Back reflection ultrasonic monitoring detected crack initiation and propagation and revealed that crack initiation is the rate-controlling step consuming about 90 percent of the total time to failure. The cracks were shown to initiate at several sites.

The effects of explosive and conventional forming on the stress-corrosion-cracking behavior of 2014 aluminum alloy have been investigated at the University of Denver.(7) Evaluations were based on exposing constant deflection bent-beam specimens stressed at 75 or 90 percent of the yield strength in the 3.5 percent NaCl alternate immersion test. Neither method of forming impaired the relatively high resistance of 2014-O alloy to stress-corrosion crack-

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ing. Explosive forming was less detrimental to the stress-corrosion-cracking resistance of 2014-T6 alloy than was conventional forming. Neither type of forming affected the stress-corrosion characteristics of 2014-T6 aluminum formed in the -O condition prior to solution treatment and aging.

FERROUS ALLOYS

Steels

The results of a questionnaire on the corrosion protection of high-strength-steel landing-gear components have been issued by Committee T-9B of the National Association of Corrosion Engineers.[8] No single best way was found to avoid the problem of brittle failure caused by hydrogen or stress-corrosion cracking. Pertinent facts, advantages, and disadvantages of the three protective systems now being used were discussed. These systems are:

(1) Paint over bare steel

(2) Paint over porous cadmium plating on steel

(3) Paint over vacuum-deposited cadmium plating on steel.

The results of 4 years' exposure to marine environments of medium- and high-strength steels have been reported by United States Steel.[9,10] Specimens were exposed to flowing and quiescent seawater (tidal zone) and in the atmosphere. The former was the most severe condition and the latter was least severe. Wrought specimens of HY-80 and HY-130 steels corroded uniformly and, after the initial year, the corrosion rates were constant at about 6.1 and 3.0 mils per year in flowing and quiescent seawater, respectively. For welded specimens, the weldments corroded more and the heat-affected zone corroded less than the base metal when immersed in seawater. Stressed specimens of these two alloys did not exhibit stress-corrosion cracking. The 12Ni-5Cr-3Mo high-strength steel (180/210 ksi yield strength) corroded at rates of 0.3 to 0.6 mil per year as determined by weight loss, but pitted at the rate of 3 to 4 mils per year. Welded specimens of this alloy exhibited rows of pits on either side of the weldment in the heat-affected zone.

The results of 16 years' exposure of steels and cast irons to tropical fresh water and seawater have been reported by the Naval Research Laboratory.[11] The fresh-water corrosion rates of carbon steel exhibited a parabolic behavior varying from an average of 7.4 mils per year in the first year to 0.7 mil per year for the time interval of 8 to 16 years. Pitting followed the same general behavior but at a higher rate, varying from an average maximum depth of 21 mils per year in the first year to about 0.5 mil per year over 8 to 16 years. Seawater corrosion rates of carbon steel became linear at 2.7 mils per year after 1 to 2 years' exposure. Pitting rates changed from 25 to 35 mils per year in the first 2 years to an eventual slope approximately parallel to that of the corrosion rate at about 3 mils per year. Of all the alloys tested, only 18-percent-nickel cast iron was more corrosion resistant than carbon steel.

Stainless Steels

The susceptibility of ferritic stainless steels to intergranular attack has been investigated at Climax Molybdenum.[12] Heating to greater than 1700 F followed by rapid cooling sensitized a number of alloys to intergranular corrosion in boiling 65 percent HNO_3 and the modified Strauss Tests. In experimental alloys, columbium additions of about 8 times the combined carbon and nitrogen content minimized intergranular attack even under highly oxidizing conditions. Titanium additions of about 6 times the combined carbon and nitrogen content were effective in preventing intergranular attack as long as the solution was not strongly oxidizing. Alloys containing molybdenum additions were most resistant to intergranular attack when rapidly quenched from 1500 F. Nickel additions to 2 percent raised the temperature required to obtain sensitization, but provided no protection against intergranular corrosion of as-welded metal.

Surface treatments with lithium silicate have prevented stress-corrosion cracking of sensitized- and intergranularly corroded Type 304 stainless steel in studies conducted at the Du Pont Savannah River Laboratory.[13] The corrodent was 90 C (194 F) water adjusted to pH 4.5 HNO_3 and containing 20 ppm chloride. Sensitized samples were overpickled in HNO_3-HF, stressed, and given one of the following treatments in 25 weight percent lithium silicate:

(1) None

(2) Dipped, rinsed, and air dried

(3) Dipped and air dried (no rinse)

(4) Boiled 0.5 hour in saturated NaCl solution, dipped in lithium silicate, rinsed, and dried

(5) Boiled 0.5 hour in saturated NaCl, dipped in lithium silicate, and air dried, no rinse.

Upon exposure to the test medium at 90 C, cracks developed within 48 hours in the untreated samples. After 890 hours' exposure, there were cracks in one of eight of the NaCl dipped-and-rinsed samples and in none of eight of the other treatments (total exposure 890 hours). The silicate also prevented rusting of the sensitized stainless steel.

NICKEL-BASE ALLOYS

Tensile tests have been performed by Rocketdyne on Alloy 718 and Ti-6Al-4V alloy specimens in hydrogen at pressures to 2000 psi.[14] In 2000 psi hydrogen, the notch tensile strength of Alloy 718 was reduced 15 percent at 140 F and room temperature and near zero at -109 F, and -320 F. The 1000-cycle fatigue strength of precracked Alloy 718 specimens was 22 percent less in 2000 psi hydrogen than in 2000 psi helium. In 2000 psi hydrogen, the notch tensile strength of Ti-6Al-4V alloy was reduced 45 percent at room temperature, 8 percent at -109 F, and zero at -320 F.

The Naval Radiological Defense Laboratory has studied the corrosion behavior of Hastelloy C in hot seawater vapor (200 C), high hydrostatic pressure (7000 psi), or ionizing radiation (2×10^5 R per hour), to predict the corrosion life of the SNAP-21 fuel container should an accident cause it to be contacted by seawater.[15] Compared with corrosion behavior in seawater at 23 C, the hot seawater vapor caused an increase in the corrosion rate

of two orders of magnitude and the hydrostatic pressure caused an increase in the corrosion rate of one order of magnitude. However, the maximum predicted corrosion rate was 7.4×10^{-4} mils per year which for a 0.25-inch-thick container shell extrapolated to a life of 3.2×10^5 years. A conclusion of the study was that this corrosion rate could easily be tolerated based on the relatively short half-life of 28 years for the radioisotopic fuel.

TITANIUM

Reaction with Hydrogen

The reactivity of Ti-6Al-4V alloy with hydrogen has been determined in the temperature range 75 to -423 F by McDonnell Douglas.(16) Precracked specimens were fatigue tested in tension-tension (12.5 to 62.5 ksi) in 1 atmosphere of high-purity hydrogen. Reactions between hydrogen and Ti-6Al-4V alloy occurred over the 75 to -100 F temperature range in the form of hydrogen absorption at the crack interface, acceleration of the crack propagation rate, and a change in the fracture mode. The fracture surfaces of the latter contained deep cracks at the fatigue striations and extensive secondary cracking. No indications of hydrogen reactions were observed in the -100 to -423 F temperature range.

Stress-Corrosion Cracking

Results of 1 year's research on the mechanism of stress-corrosion cracking of titanium alloys in aqueous solutions have been summarized by McDonnell Douglas.(17) Studies were made with alpha and alpha-beta alloys using single-edge notch specimens exposed to aqueous salt solutions at ambient temperature. Alpha-beta alloys solution-annealed or forged slightly below or above the beta transus and then rapidly air-cooled developed martensitic structures that exhibited high fracture toughness and were resistant to stress-corrosion cracking. The immunity was attributed to restricted dislocation movement in alpha by retained beta platelets. Aging of beta-forged material (Ti-8Al-1Mo-1V) at 900 to 1200 F reduced fracture toughness and increased the susceptibility to stress-corrosion cracking.

The effect of 0.01 to 1000 ppm additions of palladium, gold, ferric, or cupric ions to methanol-HCl solutions on the stress-corrosion cracking behavior of unalloyed titanium has been studied at Martin Marietta's Research Institute for Advanced Studies.(18) All caused substantial increases in susceptibility to stress-corrosion cracking and intergranular corrosion. Palladium and gold were deposited as metal films on the titanium. These films apparently facilitated the overall cathodic process by the cathodic discharge of hydrogen. The ferric and cupric ions probably facilitated the overall cathodic process by providing an additional reaction,

$$M^{n+} + e \longrightarrow M^{(n-1)+}.$$

The long-term hot-salt stress-corrosion cracking of Ti-6Al-4V alloy has been studied at Langley Research Center.(19) Self-stressed specimens at 25 and 50 ksi were sprayed with 3.4 percent NaCl solution and exposed up to 10,000 hours at 500, 550, and 600 F. Cracks initiated at 600 F within 20 and 230 hours at 50 and 25 ksi, respectively, and at 550 F within 110 and 2200 hours at 50 and 25 ksi, respectively. No cracking occurred in 10,000 hours at 500 F at either stress level. A comparison with previous results for Ti-8Al-1Mo-1V alloy indicated that there was little difference in crack initiation time for the two alloys but that cracks were deeper and more extensive in the Ti-8Al-1Mo-1V than in the Ti-6Al-4V alloy.

The effect of microstructure and alloy composition on stress-corrosion-cracking behavior of alpha and alpha-plus-beta titanium alloys has been studied at Boeing.(20) Precracked specimens were exposed to 3.5 percent NaCl solution. Additions of oxygen, aluminum, or aluminum and tin restricted slip in the alpha phase and promoted stress-corrosion cracking. This susceptibility was qualitatively related to the intensity of the stress field surrounding a dislocation pileup. Treatments that reduced the alpha grain size or increased the dislocation density improved the resistance to stress-corrosion cracking. Alloying with molybdenum or vanadium also improved the resistance to cracking apparently by stabilizing the ductile beta phase. Precipitation of a fine dispersion of alpha or omega in the beta increased the susceptibility as did intermetallic compound formation in alloys containing copper or silicon.

Fatigue

The effect of outdoor exposure at elevated temperature on the fatigue life of Ti-8Al-1Mo-1V and AM-350 alloys also has been studied at Langley Research Center.(21) Constant-amplitude bending fatigue tests were conducted outdoors and indoors on central-hole (stress concentration factor 1.6) and fusion-welded sheet specimens. The outdoor specimens were maintained at 550 F except for 4 hours each night, when rain or snow fell, or for a short period twice each week when the cyclic loads were applied. Indoor tests were at room temperature. Exposure time ranged from 7 to 23 months. The outdoor environment reduced the fatigue life of all materials tested. Time to first failure outdoors was never less than one-half of that indoors. However, the median life of the outdoor central-hole AM-350 specimen was one-fifth that of the indoor specimen. No such comparisons could be made for the Ti-8Al-1Mo-1V alloy because most failures occurred outside the test section at small spot-welding arc spots.

MISCELLANEOUS

The development of a water-displacing temporary corrosion preventive for touching up breaks in paint films on aluminum components on naval aircraft has been continued at IIT Research Institute.(22) An effective preventive was developed which displaced water already present on surfaces and in crevices, prevented further access of water, protected the surface against corrosion, and was easily removed by petroleum solvents. It consisted of a natural sodium petroleum sulfonate plus a barium salt of a complex phosphate ester and a hydrocarbon soluble resin.

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